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Citation	Research on Chemical Intermediates (2008), 34(5-7): 487-494
Issue Date	2008-05
URL	http://hdl.handle.net/2433/85339
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Type	Journal Article
Textversion	author

Title

Metal oxide promoted TiO_2 catalysts for photo-assisted selective catalytic reduction of NO with NH_3

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Key Words

TiO_2, photocatalyst, SCR, transition metal oxide, NH_3, NO

Abstract

The photo-assisted selective catalytic reduction of NO with NH_3 (Photo-SCR) was performed over TiO_2 modified by supporting 1wt.% various transition metal (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ta or W) oxides aiming at the improvement of the photo-SCR activity. The addition of Nb, Mo or W oxide to TiO_2 was found to enhance the photo-SCR activity. We have reported that the amount of acid sites on TiO_2 is one of the key factors to the photo-SCR activity. The increase in the activity depends on the enhancement of acidity of catalyst by the addition of Nb, Mo or W oxide. On the contrary, the addition of V, Cr, Mn, Fe, Co, Ni or Cu oxide to TiO_2 lowered the photo-SCR activity although addition of metal cations also change the acidity of TiO_2. We guess that the reduction of the activity was caused by two reasons; the first is that the sites newly formed on these transition metal oxides is not photoactive and the second is that TiO_2 supporting V, Cr, Mn, Fe, Co, Ni or Cu oxides had low stabilities under the reaction condition, i.e., the chemical state of the cations changes during the reaction. Therefore, we concluded that the increase in the acid sites which is active sites for photo-SCR and the stability of the catalysts are important for the photo-SCR.

1. Introduction

NO*x* is an air pollutant and causes town smog and acid rain. It is important to remove NO*x* exhausted in the stationary emission source and mobile emission source. In the stationary emission source, such as a power station, waste incinerator and an industrial boiler, NO*x* is removed by an efficient technology of selective catalytic reduction (SCR) with NH_3 in the presence of O_2. Industrial SCR systems are carried out over V_2O_5-WO_3/TiO_2 or V_2O_5-MoO_3/TiO_2 catalysts at 573-673 K[1-4]. The SCR process is often located at downstream of the desulfurizer, dehalogenizer and electrostatic precipitators where SO*x*, halogen compounds and ash are removed because these materials cause the deactivation of catalyst. Since the emission gas temperature in the downstream is below 423 K, it is necessary to develop SCR system operated at low temperature without re-heating the fuel gas[5-7].

We paid attention to photocatalyst operated at low temperature in order to develop low temperature SCR system. We have already reported that photo-SCR of NO with NH_3 in the presence of O_2 proceeds at room temperature over Rb-ion-modified vanadium oxide supported on silica (Rb_2O-V_2O_5/SiO_2)[8], titanium oxide supported on silica (TiO_2/SiO_2)[9] and titanium dioxide (TiO_2)[10, 11] under irradiation. When TiO_2 is used as a catalyst, 83% of NO conversion and 96% of N_2 selectivity can be achieved in the conventional fixed bed flow system at 8,000 h^{-1} [12]. However, this photo-SCR activity is low in comparison with industrial SCR system and it is necessary to increase the photo-SCR activity.

We have reported that the acid sites on TiO_2 are active sites for the photo-SCR reaction and the activity depends on the amount of the acid sites[10]. Therefore, it is expected that the enhancement of the acidity of the catalyst improves the activity. The addition of the transition metal oxide to the supports (metal oxides) often generates the

further surface acidity because of an increase in the polarizability in the supports modified with the transition metal oxide[13]. Some researchers reported that the acidity of TiO_2 was enhanced and the acid property of TiO_2 was changed by the addition of transition metal oxides (W, Mo, V, Fe, Mn, Cr or Cu oxide) [6, 7, 13]. Recently, some transition metal supporting catalysts, such as MnO_x/Al_2O_3[14], MnO_x/TiO_2[6], CuO/Al_2O_3[15], CuO/TiO_2[16] and Fe_2O_3/TiO_2[17], have showed high activities for the low temperature SCR systems. The high activity in these reaction systems is thought to be due to an increase of active sites, the enhancement of the interaction between catalyst and substrate, and improvement of the stability by supported transition metal. In the present work, we carried out photo-SCR of NO with NH_3 over TiO_2 promoted with various transition metal oxides and contributed the development of active catalyst in the photo-SCR.

2. Experimental

TiO_2 used in this study is Super Titania F-6 (Lot No.H04320) kindly supplied from SHOWA DENKO. This sample was hydrated in distilled water at 353 K for 2 h and filtered with suction, followed by dryness at 383 K over night. Dried sample was calcined in dry air at 673 K for 3 h. Thus prepared TiO_2 exhibited a specific surface area of 76.6 m^2/g determined by N_2 adsorption. The crystal phases of this sample were 91.3% anatase and 8.7% rutile determined by SHIMADZU XD-D1 X-ray diffractometer using Cu Kα radiation. The TiO_2 catalysts promoted with various transition metal oxides were prepared by the wet impregnation followed by evaporation to dryness. Super Titania F-6 were impregnated with aqueous solutions of various transition metal precursors (showen in Table 1) at 353 K and concentrated at 353 K. After these samples were dried at 383 K over night, these were calcined in dry air at 673 K for 3 h.

Photo-SCR activity measurements were carried out in a conventional fixed bed flow system at room temperature. Catalysts were fixed with quartz wool and filled a quartz reactor which had flat facet (12 x 10 x 1 mm^3). Before reactions, catalysts were pretreated at 673 K by flowing 10% O_2 diluted with Ar at 50 ml/min. The typical reaction gas composition was as follows: NH_3: 1000ppm, NO: 1000ppm, O_2: 2%, Ar balance. PERKIN-ELMER PE300BF 300 W Xe lamp was used as a light source and samples were irradiated from the one side of the flat facets of the reactor with this lamp. N_2 and N_2O products were analyzed by a SHIMADSU GC-8A TCD gas chromatograph with MS-5A column for N_2 detection and Chromosorb 103 for N_2O. The photo-SCR was carried out in the low active condition (GHSV = 50,000 h^{-1}) in order to that the activity is not saturated.

3. Result and Discussion

Table 1 shows the photo-SCR activities of TiO_2 and various transition metal oxide promoted TiO_2 catalysts. 42.4 % NO conversion was obtained on pure TiO_2 and traced N_2O was detected over only TiO_2 promoted Nb, Mo or W oxide catalysts. The activities of Zn, Y, Zr or Ta oxide added to TiO_2 samples were nearly equal to the activity of pure TiO_2. The addition of Nb, W or Mo enhanced the photo-SCR, and it was found that 1wt.% WO_3/TiO_2 was the most active catalyst (63.6 % NO conversion) in all samples. On the other hand, V, Cr, Mn, Fe, Co, Ni, or Cu oxide addition to TiO_2 catalysts exhibited lower activities than pure TiO_2. We have already reported that the active site of photo-SCR is acid site on TiO_2[11] and acidity of the catalyst is an important factor to determine the photo-SCR activity[12]. It is known that the amount of acid sites on a metal oxide is often increased by addition of other transition metal (V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W et al.) oxides[6, 13, 16]. It is likely that an increase of active sites enhances the photo-SCR activities. In fact, the addition of Nb, Mo or W oxide to TiO_2 samples enhanced the photo-SCR activity. However, the addition of V, Cr, Mn, Fe, Co, Ni, or Cu oxides exhibited the negative effect for photo-SCR, although these transition oxides adding to TiO_2 catalysts might also increase the acidity[6, 13, 16]. These results suggest that the amount of acid sites is not only the factor in the photo-SCR.

There were several reports that the selective catalytic reduction of NO with NH_3 at 393-623 K was enhanced by using Mn, V, Fe, Cu oxide supported on TiO_2 catalysts[6, 14, 16-18]. In these SCR systems, almost unanimously it is thought that reaction occurs on the transition metal cationic centre (acid site), where both ammonia and NO can be adsorbed[4]. However, Mn, V, Fe and Cu oxide promoted catalysts showed low activities in the present case, indicating that active sites in the photo-SCR are not the transition metal cationic centre but the acid sites on TiO_2. In addition, the activity followed the order V > Cr > Mo≥ W in low temperature SCR [18], while in the present photo-SCR the activity followed the order W > Mo > Cr > V. We speculate that the reason why the activities of

V, Cr, Mn, Fe, Co, Ni, Cu oxide promoted catalysts were lower than that of pure TiO_2 is that the active sites on TiO_2 is covered with these transition metal oxides, resulting in the formation of acid sites on themselves.

It is thought that the stability of the catalyst under photo-reaction is important for this reaction. Fig. 1 shows the time courses of the photo-SCR reaction at GHSV = 50,000 h^{-1} over pure TiO_2, 1wt.% CrO_2/TiO_2, 1wt.% ZrO_2/TiO_2 and 1wt.% WO_3/TiO_2, whose activities were lower, the same and higher catalysts than pure TiO_2 respectively for example. In the cases of pure TiO_2, 1wt.% ZrO_2/TiO_2 and 1wt.% WO_3/TiO_2, the photo-SCR activity reached to the steady state activity for 30-60 min without deactivation and we confirmed that this activity was kept for at least 15 h. Same results were obtained over Zn, Y, Ta, Nb or Mo promoted TiO_2 catalyst. On the other hand, in the case of 1wt.% CrO_3/TiO_2, the photo-SCR activity decreased as the time going on and after that, the activity reached to the steady state. V, Mn, Fe, Co, Ni, or Cu oxide addition to TiO_2 catalysts, which showed the lower activities than pure TiO_2, exhibited the similar behaviours to Cr oxide supported catalyst. It is thought that this deactivation depends on the low stability of the catalysts under photo-reaction. It was reported that TiO_2 supported Mn, Cr, Co or Cu oxide catalysts came under the influence of water under the SCR reaction and the activity decreased as the increase in the water concentration[7]. The stoichiometric equation of the photo-SCR is displayed as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

The produced water in the photo-SCR would affect the photo-SCR activity and make the activity reduced as well as in the cases of the reported SCR systems[19]. Moreover, UV-Vis-NIR spectra of TiO_2 supported Cr or Cu oxide catalysts revealed that the states of Cr and Cu oxides were altered by the photo-SCR reaction. Fig. 2 shows the UV-Vis-NIR spectra of TiO_2 supported Cr or Cu oxide catalysts before and after reaction. The TiO_2 supported Cr oxide before reaction showed three absorption bands centred at 290, 433 and 664 nm. After photo-SCR reaction, the intensities of the absorption bands at 290 and 454

nm decreased and that of the band at 600-800 nm increased. A CrO_3 crystallite consisted from Cr^{6+} which has tetrahedral structure exhibits two LMCT bands at 280 and 400 nm[20]. A Cr_2O_3 crystallite which has octahedral Cr^{3+} shows a large d-d transition band in the region of 600-800 nm. The change of UV-Vis-NIR spectrum by the photo-reaction indicates that Cr^{6+} species on the catalyst was reduced and Cr^{3+} species was formed. The same alternation was observed at Cu oxide supported on TiO_2 catalyst. The UV-Vis-NIR spectrum before reaction (Fig. 2b) showed that two absorption bands in the region of 250-400 nm and 600-1200 nm. Both a $Cu(OH)_2$ and a $CuAl_2O_4$ crystallites which have octahedral and tetrahedral Cu^{2+} species respectively exhibit absorption band in the region of 600-1400 nm[21]. On the other hand, Cu_2O which has Cu^+ species show a band gap direct transition around 510 nm. In Fig. 2b, the absorbance at 400-600 nm increased and that at 600-1200 nm decrease after the photo-SCR reaction. This alternation indicates that Cu^{2+} species declined and Cu^+ species was generated under photo-SCR condition. These results indicate that Cr or Cu oxide added to TiO_2 catalysts are not stable under photo-SCR condition and the reduction of Cr^{6+} and Cu^{2+} is one of the deactivation factor. On the other hand, not only W oxide but also Mo and Nb oxide promoted TiO_2 catalysts were stable for photo-SCR reaction. It is reported that Mo and W oxides act as both stabilizers and promoter of catalysts[4]. Nb oxide is reported to promote the catalytic activity as a support for metal oxides[22]. Therefore, the promotion of Nb, Mo and W oxides to TiO_2 may increase the stability of TiO_2 and this stability under photo-reaction prevents the activity from the attrition.

Moreover, W and Mo oxides are known to result in the formation of the acid sites on zirconia or titania[13, 23]. We determined the amount of acid sites of the catalyst by NH_3 adsorption amount. We confirmed that the amount of acid sites of TiO_2 (0.42 mmol g^{-1}) increased by the addition of Nb (0.46 mmol g^{-1}), Mo (0.50 mmol g^{-1}) or W (0.44 mmol g^{-1}) oxide. We have demonstrated that the active site of the photo-SCR is the acid site on the catalyst. This increase of the acidity caused by the promotion of Nb, Mo or W

oxide to TiO_2 made the activity enhanced. We concluded that both the stability and the acidity of the catalyst are important factor for the photo-SCR.

Fig. 3 shows the NO conversion and N_2 selectivity as a function of GHSV over 1wt.% WO_3/TiO_2 in the photo-SCR. 1wt.% WO_3/TiO_2, which showed the highest activity in this study, exhibited 92% NO conversion and 99% N_2 selectivity at GHSV = 16,000 h^{-1}. At present, it is necessary of the development of SCR system, which has above 90% NO conversion and high N_2 selectivity and is operated at $\leq$ 423 K at high GHSV value[5-7]. Our photo-SCR system operated at room temperature under UV irradiation fills these demands and is available for the low temperature SCR system.

4. Conclusion

We carried out the photo-SCR at room temperature over TiO_2 promoted by various transition metal oxides. The addition of Nb, Mo or W oxides to TiO_2 enhanced the photo-SCR activity although the addition of V, Cr, Mn, Fe, Co, Ni, or Cu oxides gave the negative effect to the photo-SCR activity. The promoters of Nb, Mo and W oxides contribute to the enhancements of the stability and the acidity of catalyst and we concluded that these enhancements led the increase in the photo-SCR activity. Moreover, 1wt.% WO_3/TiO_2 catalyst exhibited 92% NO conversion and 99% N_2 selectivity at GHSV = 16,000 h^{-1}. The catalyst we found in this study would be available at the practical level for the low temperature SCR.

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Table 1 Precursors of loading metal oxides and results of photo-SCR of NO with NH_3 over various catalysts.

Catalysts	Precursors	NO conversion / %	N_2 selectivity / %
TiO_2	—	42.4	100
1wt.% V_2O_5/TiO_2	Ammonium Vanadate	17.7	100
1wt.% CrO_6/TiO_2	Chromium Nitrate	34.2	100
1wt.% MnO/TiO_2	Manganese Chloride	12.1	100
1wt.% Fe_2O_3/TiO_2	Iron Nitrate	29.6	100
1wt.% CoO/TiO_2	Cobalt Acetate	21.6	100
1wt.% NiO/TiO_2	Nickel Chloride	27.0	100
1wt.% CuO/TiO_2	Copper Nitrate	26.1	100
1wt.% ZnO/TiO_2	Zinc Acetate	46.6	100
1wt.% Y_2O_3/TiO_2	Yttrium Nitrate	47.0	100
1wt.% ZrO_2/TiO_2	Zirconium Nitrate	41.1	100
1wt.% Nb_2O_5/TiO_2	Ammonium Niobium Oxalate	58.4	>99
1wt.% MoO_3/TiO_2	Hexa-Ammonium Heptamolybdate	60.2	>99
1wt.% Ta_2O_3/TiO_2	Tantalum Chloride	38.6	100
1wt.% WO_3/TiO_2	Ammonium Tangstate	63.6	>99

Reaction condition; NO: 1000ppm, NH_3: 1000ppm, O_2: 2%, Ar balance, GHSV: 50,000 h^{-1}.

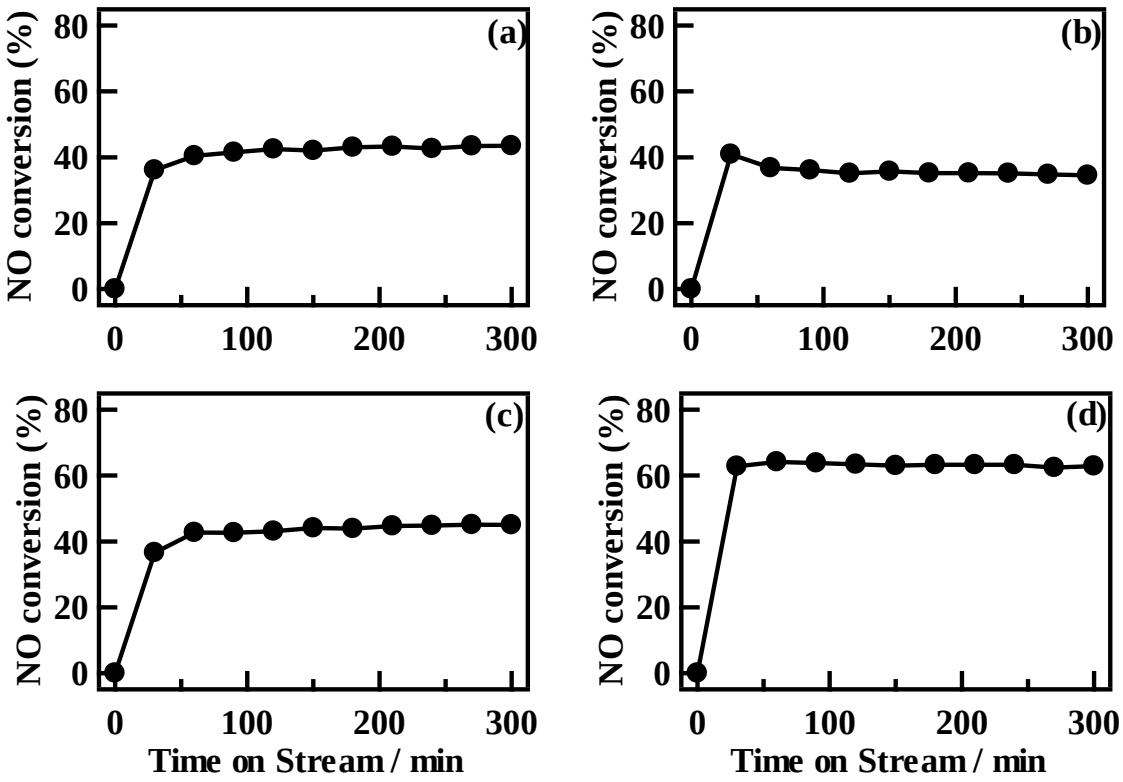

Fig. 1 Time courses of the photo-SCR reactions over (a)TiO_2, (b)1wt.%CrO_3/TiO_2, (c)1wt.%ZrO_2/TiO_2 and (d)1wt.%WO_3/TiO_2 at GHSV = 50,000 h^{-1}. Reaction condition; NO: 1000ppm, NH_3: 1000ppm, O_2: 2%, Ar balance.

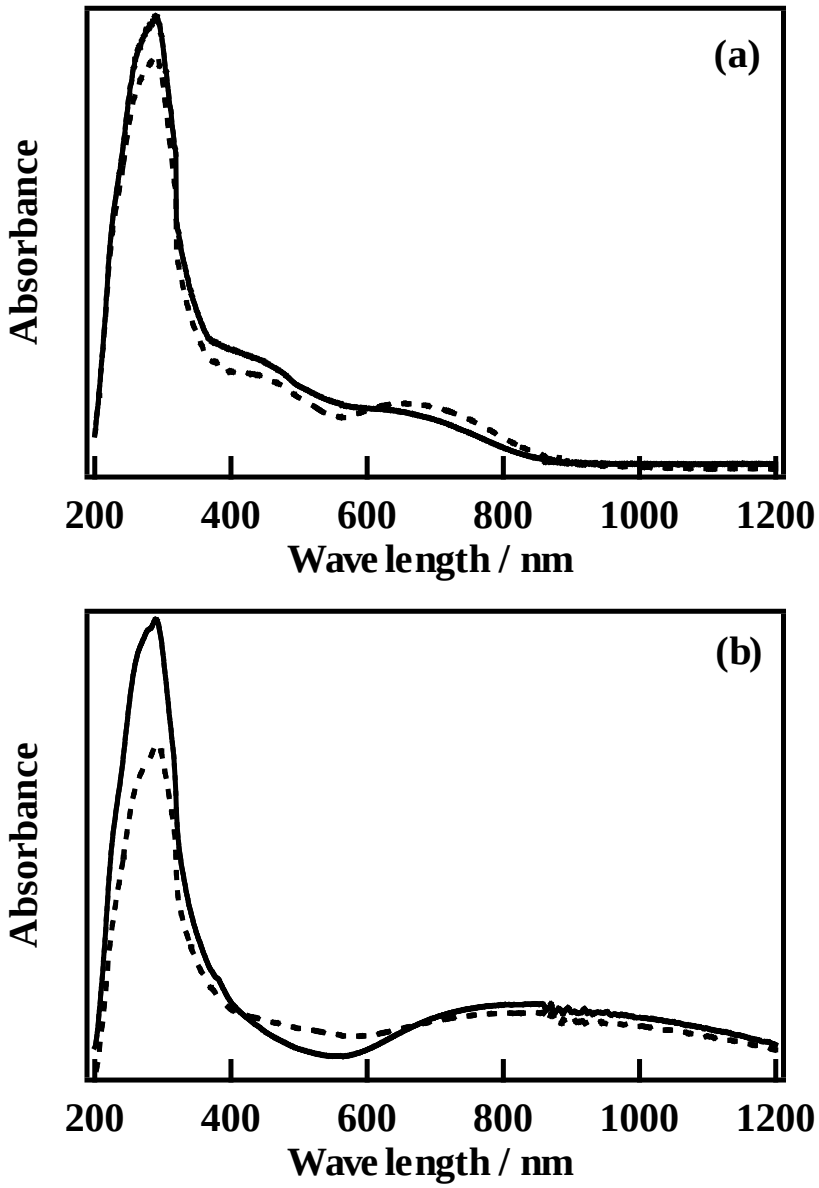

Fig. 2 UV-Vis-NIR spectra of (a)1wt.%CrO_3/TiO_2 and (b)1wt.%CuO/TiO_2 before (solid line) and after (broken line) reaction.

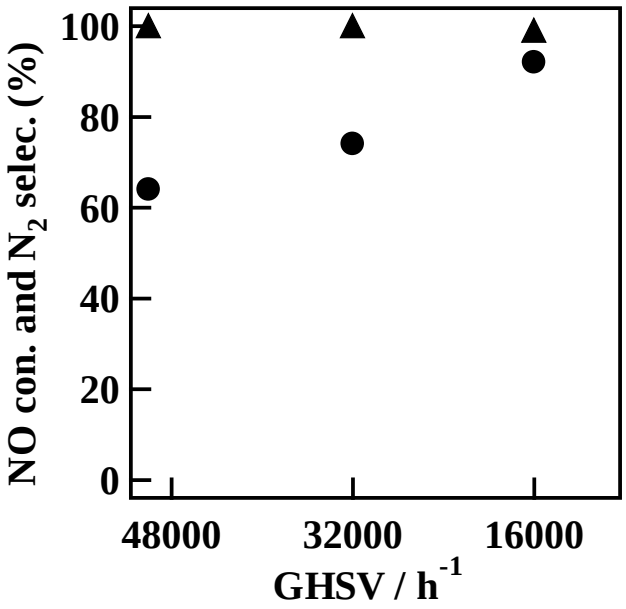

Fig. 3 NO conversion and N_2 selectivity at some GHSV over 1wt.% WO_3/TiO_2. Reaction condition; NO: 1000ppm, NH_3: 1000ppm, O_2: 2%, Ar balance. ● NO conversion, ▲: N_2 selectivity.